Rec'd PCT/PTO 20 JUN 2005

PROCESS FOR MANUFACTURING RETROREFLECTIVE PRINTED MATERIAL

DESCRIPTION

The present invention refers to a process for manufacturing retroreflective printed material.

It is known that retroreflective products used for safety garments can reduce risk of accidents, especially for some particular categories of people, such as, for example: firemen, paramedicals, adult and children playing sports.

The only commercial products suitable for reflective garments have generally been of the single-colored type. For example in US-A-4.763.98, US-A-5.283.101 and US-A-5.738.746 launderable retroreflective grey-colored products are disclosed. The following patents describe the possibility of obtaining colored effects and printed effects as well as reflective quality.

A retroreflective structure described in US-A-5.962.121 is capable of exhibiting a decorative effect both during the day and during the night, and particularly a rainbow-colored effect .

In US-A-4.605.461 a method is described for transferring a retroreflective pattern onto a fabric. Retroreflective images formed on garments and other substrates are described in US-A-4.102.562, while US-A-5.508.105 discloses a thermal printing system and a colorant/binder for printing frangible, retroreflective sheeting material. US-A-5.620.613 discloses printing of designs or emblems on garments, comprising a monolayer of

microspheres and a first printing of the first color layer with a silk-screening system. When the prints of the first color are all dried, the subsequent colors can be printed through the same technique until the design on the layer of microspheres is completed. A similar patent for decorating textile surfaces, US-A-5.679.198, discloses a multi-step printing of many colors prepared with a polyester resin and an isocyanate hardener, dried before printing the following color and so on. Also in US-A-5.785.790 the same silk-screening multi-color printing technique is used with a system of colors made of polyester resin hardened with isiocyanate.

Many other patents (US-A-3.689.346, US-A-5.643.400, US-A-4.082.426, US-A-2.231.139, US-A-2.422.256, US-A-4.656.072, US-A-4.952.023) describe processes for producing retroreflective materials. US-A-6.120.636 discloses a high speed, low cost process for producing sheets patterned with drawings and emblems using a rotary screen printing system with cylinders and hardening with U.V. lamps.

Despite the above-described prior art situation, there still remain restrictive limits for printing retroreflecting products using many colors, with a high production speed, production flexibility and without ecological problems. From what is known, no one has previously found a practical way to produce a printed retroreflective product for fashion use using designs containing one or many colors. Some have proposed silk-screen printing with one water-based color or solvent-based colors but the above inventions are unfeasible for reproducing fashion designs with many colors upon a retroreflective material.

In the present invention as pointed out in Claim 1, a temporary support sheet is provided, with a monolayer of transparent glass microspheres partially embedded in a layer of softened polymer to a depth ranging between one-quarter and one-half of the microsphere diameter, as conventionally used in retroreflective materials, as described in US-A-3.700.305 and US-A-6.416.188. Then, after coating the layer of microspheres with a thin thermo-adhesive polymer film, a design is thermo-transferred onto the microsphere surface.

Two kinds of commercial transfer-printed design may be used:

(a) designs with sublimate pigments printed on a paper base; or

(b) designs having a polymer film supported by a release paper base or a polymer film base, such as for example a film of polypropylene.

In case of transferring a printing with sublimate pigments (a), the transfer temperature ranges between 180°C and 220°C. A temperature close to 220°C causes a maximum yield of color transferring, but also a partial transferring of colors at lower temperatures may give a satisfactory aesthetic design on the final retroreflective product.

In case of transferring a printed polymer film as shown in (b), the layer of microspheres is beforehand coated with a thin layer of bicomponent polyurethane. The thin layer of polyurethane resin dried but not cured operates as thermo-adhesive between microspheres and printed film. In this case, the print transfer temperature is lower than 150°C, and preferably between 100°C and 120°C.

As regards the above-described prior art, many patents use the screen-printing technology (US-A-5.620.630, US-A-5.785.790 and others). With this printing system, it is concretely impossible to print designs containing many colors while maintaining the design accuracy and the perfect fitting of various printed colors, not as is normally done on a textile support but on a layer of microspheres to produce retroreflecting materials. The same considerations can be done with a rotary screen-printing system (US-A-6.120.636).

The present invention instead provides a flexible, ecological, easy-to-apply process, for obtaining printed retroreflective products especially, but not restrictively, for fashion garments where rich designs and colors are demanded and appreciated. The printing transfer machine needs a low-cost investment compared with other printing processes; no auxiliary equipment and small floor space are required, and no pollution or obnoxious effluence is produced. Moreover, the availability of commercial transfer printed papers is considerable.

A special feature of the present invention is the possibility of vacuum application of a thin aluminium reflecting layer after the printing process. In this case, it is possible to avoid the application of a transparent dielectric mirror though maintaining a sufficient reflective intensity for a printed fashion product.

Over the printing or over the reflective aluminium layer, a polyurethane two-components resin is coated, dried and laminated over a fabric. The polyurethane resin coating may be substituted with a thin layer of a hot-melt adhesive being applied.

The present invention will be better described by some preferred embodiments thereof, provided as a non-

limiting example, with reference to the enclosed drawings, in which:

- Figure 1 shows a schematic sectional view of an article of clothing 10 at the final stage of production according to the present invention ;
- Figure 2 shows a schematic view of a continuous apparatus for doctor blade on roll coating of a supported layer of microspheres;
- Figure 3 shows a schematic view of a production machine for transferring printed designs using sublimation pigments;
- Figure 4 shows a schematic carrier web, which secures microspheres thereon in a desired temporary arrangement;
- Figure 5 is a plan view showing a schematic design of a printed paper; and
- Figure 6 schematically shows the drawing transfer of Fig. 5 from the original printed sheet to the surface of the layer of microspheres.

In the invention as described and shown, a specific terminology is used for better clarity. However, the invention is not constrained to the specific terms being chosen and it is obvious that every chosen term comprises every technical equivalent that generates a similar behaviour.

Fig. 4 is a cross sectional view of a carrier web 20, which secures glass microspheres 1 on a temporary transport support. The carrier web used as a sheet material is produced as described in US-A-4.102.562. The microspheres 1 used in the present invention typically have an average diameter in the range of about 30 to 200 microns and a refractive index of about 1.7 to 2.0. Preferably the glass microspheres 1 are arranged

substantially in a monolayer on a temporary carrier sheet 20, which comprises a backing sheet 3 and a polymeric coating film 2. The polymeric coating 2 is a softenable material such as polyethylene, polypropylene and the like. The stiff backing sheet 3 could be kraft paper, polyester film and the like.

The microspheres 1 may be arranged upon the temporary carrier sheet 20 by printing, cascading, transferring, and screening or any convenient transfer process.

The microspheres 1 can be embedded in the carrier sheet 20 with a pressure roll or by heating the softened polymer, to a depth between about 20% to 40% of their average diameter.

Fig. 1 shows a sectional view, not to scale, of a portion of an article of clothing 10 that is partially delaminated from the carrier web comprising the polymeric coating 2 and the kraft paper or polyester film backing 3.

Disposed adjacent to the non-embedded glass surface of the microspheres 1 is a transparent dielectric mirror 4, a priming layer 5 of bi-component polyurethane of about 1 micron.

The layer 6 reduces the printed layer, whose thickness is less than 0.1 microns, in the case of sublimate pigments (a) and less than 0.5 microns in the case of transfer printing supported by a polymer film (b).

With reference again to Fig. 1, the printed design over the microspheres 1 is covered with a layer 7 made of vacuum-nebulised aluminium, or other light reflecting material. Obviously, in this case the layer of transparent dielectric mirror 4 is not necessary.

With reference again to Fig. 1, finally, a binder layer 8 will provide an adequate thermal adhesion with a base fabric 9, for example a polyester/cotton fabric, a

nylon knitted fabric made of a Lycra® or other textile bases.

Fig. 2 and 3 are schematic drawings of apparatus used in the invention, which include a well-known rotary machine 29 for thermal transfer printing of the calender type (manufactured by Lemaire, Roubaix, France or Monti Officine, Thiene, Italy).

The composite microspheres layer 33 (supplied by cylinder 40), as described in Fig. 4, together with the printed paper 30 (supplied by cylinder 24) are pressed between heated cylinder 27 and felt 26 in a continuous process (Fig. 3). Out of the machine, the paper 31 without the design is wound on cylinder 25 on one side, and the printed layer of microspheres 34 is wound on cylinder 32 on the other side.

In Fig. 2 the continuous printing process is made on the composite material 33 (supplied by cylinder 40) coated (in machine 23) with a polyurethane layer 5 (supplied by cylinder 22) as shown in Fig. 3. At the end of the process, a product 34 is obtained that is wound on cylinder 28.

Fig. 5 is a schematic plan view showing a transfer paper 30 printed with nature image containing 8 colors a, b, c, d, e, and f. The commercial offer of transfer printed paper is remarkable. This type of paper is widely used in many applications in textile industries but also in several areas such as accessories, furniture, interior decorations, motor vehicles and the like.

Samples of the present invention have been prepared using transfer printed papers from Transfertex GmbH, Kleinostheim, Germany and a special polypropylene printed film Decotrans® from Miroglio Sublitex, Alba, Italy.

Fig. 6 is view of partially removed released paper 31 without the design from the carrier web, which secures microspheres covered with the printed transferred image 34.

The invention will be further explained by the following illustrative examples, which serve the purpose of showing the features and advantages of this invention. However, the ingredients and the specific amounts recited therein, as well as other conditions and details are intended to be not limiting of the scope of the present invention. Unless otherwise specified, all amounts are expressed in the examples are in parts by weight.

EXAMPLE 1

Cascading the microspheres on a Kraft paper covered with an acrylic auto-adhesive film produced the monolayer of glass microspheres having diameters between 40 and 100 microns. The layer of microspheres was then transferred onto a support sheet of polyester covered with a low-density polyethylene thermo-adhesive film of 50-micron thickness. The transfer was made with a heated calender as shown in Fig. 3 at a cylinder temperature of 140°C. The contact time was 5 seconds and the pressure between the cylinder and the felt was 5 bars, in order to obtain a penetration of the microspheres onto the polyethylene film of about 40% of their diameter. The exposed surface of the microspheres was then coated with a transparent dielectric mirror as described in US-A-3.700.305.

A bi-component polyurethane priming layer was next applied over the electric mirror, by coating a solution of the following formulation 1 with a doctor knife-coating machine or a graved-roll coating machine :

Ingredients	Parts by Weight
Polyurethane resin ("B 10" from Coim)	100
Curing agent ("Imprafix TH" from Bayer)	5
Methylethylketone	150
Formulation 1	

The resin has been dried and partially cured at 110°C. The amount of transparent film layer is about 4 g/m^2.

At the end of the oven as described in the Fig. 2, the product is running into the calendar heated at 130°C and laminated with the printed polypropylene Decotrans® design shown in Fig. 5. The contact time is about 10 sec. Then the polypropylene without the design and the printed microspheres were separately unwound.

Subsequently, a solution of the following polyurethane formulation 2, using a knife on roll coating, was coated over the printed layer at approximately a 125-micron thick wet substance:

Ingredients	Parts by Weight
Polyurethane resin ("B 10" from Coim)	100
Curing agent ("Desmodur RFE" from Bayer)	5
Methylethylketone	40
Melamine curing agent ("C6" from Coim)	3
Formulation 2	

The resin has been dried at 80°C. At the end of the oven the surface of the resin was superposed and calendered on a white polyester/cotton fabric containing 65% of polyester and 35% of cotton. After calendering the laminated compound at 100°C and a pressure of 5 bars, the compound was cooled and the polyester film was peeled off. Subsequently the printed retroreflective textile was cured at 150°C for 2 min.

EXAMPLE 2

A monolayer of glass microspheres having similar characteristics as those mentioned in Example 1 was deposited onto the low density 50-micron polyethylene film supported by a 40-micron polyester carrier. The glass spheres-covered carrier was then heated for 2-4 min at 150°-160°C and penetrated into the softened polyethylene. The glass microspheres thus became embedded in polyethylene for about 40% of the sphere diameter and formed a monolayer therein with little or no space between spheres. The coating with a transparent dielectric mirror

and the subsequent steps of production were the same as described in Example 1.

EXAMPLE 3

The monolayer of glass microspheres having diameters between 40 and 100 microns was produced by cascading the microspheres onto a thick release paper covered with an acrylic auto-adhesive film as described in Example 2 of US-A-4.075.049. The resulting microspheres binder composite was doctor-knife coated with a water polyether polyurethane dispersion having the following formulation 3:

Ingredients	Parts by Weight
Polyurethane water based resin ("Idrocap 930" from Icap)	100
Curing agent ("Icaplink X3" from Icap)	5
Water	40
Thickening agent ("Idrocap 200" from Icap)	a.r.
Formulation 3	

The amount of wet resin was about 10 g/m^2 and was adjusted with the doctor knife profile, resin dilution and viscosity. The amount of dry film was about 3 g/m^2. The resin was partially cured at 110°C.

At the end of the oven as described in Fig. 2, the product was run into the calender heated at 130 °C and

laminated with the printed polypropylene Decotrans® design shown in Fig. 5. The contact time was about 10 sec. Then the polypropylene without the design and the printed microspheres were unwound. The resulting printed composite was worked according to whether it comes covered or not covered with a vapour coating of a metal such as aluminium light reflecting material 7 in Fig. 1.

In case the composite was metallised, the subsequent process was the same as described in Example 1. In case the composite was not metalleisd, the subsequent treatment was polyurethane knife coating and textile lamination.

The printing effect without light reflecting aluminium is very regular but the average initial reflectivity was between 8 and 15 cd/(luxm), that was a low value for a technical product but that remained effective for a fashion fabric. The metal layer of the printed retroreflective fabric that was metallised favourably affects the design colors and reflectivity is greater than 50 cd/(luxm).

EXAMPLE 4

The monolayer of glass microspheres having diameters between 40 and 100 microns was produced by cascading the microspheres onto a thick release paper covered with an acrylic auto-adhesive film as described in Example 2. The exposed surface of the microspheres was then coated with a transparent dielectric mirror. Then, the transfer print process was made using a commercial transfer printed design with sublimate pigments (a) from Transfertex GmbH, Kleinostheim, Germany. The transfer temperature was about 185°C. In fact the heated roll was in contact with the back of the transfer paper, therefore the real temperature of the glass layer was higher than the real temperature of the printed paper but sufficient for obtaining a good

yield of pigments sublimation onto the upper surface of the microspheres. The composite material was metallised and coated using Formulation 2 with a knife on roll coating machine. The resin dried at 80°C. At the end of the oven the surface of the still tacky resin was superposed and calendered on a white polyester/cotton fabric containing 65% of polyester and 35% of cotton. After calendering the laminated compound at 100°C and a pressure of 5 bars, the compound was cooled and the polyester film was peeled off. Subsequently the printed retroreflective textile was cured at 150°C in an oven for about 2 min for finally curing the resin.